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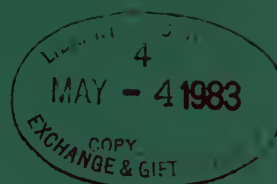
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Aluminum From Domestic Clay Via a Chloride Process

The State-of-the-Art

By A. Landsberg



UNITED STATES DEPARTMENT OF THE INTERIOR

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James G. Watt, Secretary

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

atm	atmosphere	kcal	kilocalorie
Btu	British thermal unit	lb	pound
° C	degree Celsius	pct	percent
K	Kelvin	yr	year

ALUMINUM FROM DOMESTIC CLAY VIA A CHLORIDE PROCESS

The State-of-the-Art

By A. Landsberg ¹

ABSTRACT

Kaolinitic clays are potentially a vast domestic resource for aluminum. Utilization of this resource could decrease or eliminate the nearly complete dependence of the United States on foreign raw materials for this important metal. Furthermore, processing of clay to aluminum through anhydrous chloride metallurgy could reduce the high electrical energy requirements of the conventional Hall-Heroult aluminum reduction process. Several anhydrous chloride processes have been proposed; however, unresolved technical problems have prevented their commercialization. In particular, an acceptable chemical means has not been found to extract aluminum from clay as a highly pure anhydrous aluminum chloride. This Bureau of Mines report identifies and discusses the important chemical problems involved in achieving an acceptably rapid, self-heating, selective chlorination reaction and the subsequent separation of iron chloride byproduct from the anhydrous aluminum chloride.

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INTRODUCTION

The worldwide use of aluminum exceeds that of all other metals except iron. Fortunately, aluminum is one of the most abundant elements in the earth's crust and bauxite, the principal ore of aluminum, is plentiful and accessible to surface mining. However, the prime bauxite deposits are situated in tropical areas so that the largest producer and consumer of aluminum, the United States, must import over 90 pct of its aluminum raw material (24).²

The present commercial production of aluminum is dependent upon two processes: the Bayer process for producing pure alumina from bauxite and the Hall-Heroult process for electrolytically reducing the alumina to aluminum metal. These two processes are very energy intensive, requiring over 244 million Btu to produce 1 ton of aluminum. In comparison, only 24 million Btu are needed to produce 1 ton of steel (3). Furthermore, over two-thirds of the energy used in the aluminum industry is consumed as expensive electrical energy in the Hall-Heroult reduction process. Research and development efforts have increased the efficiency of the Hall-Heroult process since its discovery nearly 100 yr ago to the point that further major improvements are unlikely.

Producing aluminum from domestic resources with less electrical energy has been the goal of several proposed aluminum processes (15, 37). While a few of these schemes have been developed through the pilot plant scale, technical and economic realities have precluded adoption of new aluminum technologies. Nevertheless, the search continues. The success of anhydrous chloride metallurgy in the commercial-scale production of the reactive metals titanium and zirconium has provided motivation to develop an analogous chloride metallurgy for aluminum. Recent operation of pilot-plant-scale aluminum chloride reduction cells has revived interest in the chloride process for aluminum (42).

However, as is often the case with new and promising technology, factual information has often been strongly exceeded by publicity and speculation, frequently colored by a lack of technical understanding, and sometimes completely neglected in an overpowering urge to secure the benefits and rewards of a more efficient process. Therefore, it is timely that a review be made to describe the chloride metallurgy of aluminum, to evaluate recent developments, and to outline the problems that remain unresolved.

BACKGROUND

The technical literature abounds with suggested methods for making aluminum but the Hall-Heroult reduction process continues to be the commercial method used and alumina to feed the reduction cells continues to be made by the Bayer process from bauxite (14). There are good reasons for this.

First, the raw material is found in large, easily mined deposits that have been concentrated and upgraded over geologic time by the action of water.

The resulting bauxite contains alumina relatively free of impurities. Second, the established, large-scale Bayer process uses common reagents to refine this bauxite to cell-grade alumina. And finally, the purified alumina is reduced to aluminum metal in well-engineered Hall-Heroult cells. This makes up today's aluminum industry: a large-scale, highly efficient technology which has enjoyed nearly a century of development through huge investments of human effort and financial resources (13). In order to be a viable competitor any new aluminum technology must be economically superior and an almost instant technical success. Nonetheless, with current

²Underlined numbers in parentheses refer to items in the list of references at the end of the report.

TABLE 1. - Pertinent compositions, percentages

	Kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$)	Typical clay (calcined)		Jamaican bauxite dried ¹
		Georgia kaolin	Used for calculations	
Al_2O_3	39.5	40 -45	45	49
SiO_2	46.5	49 -52	51	2
Fe_2O_3	NAP	.5- 3	2	20
TiO_2	NAP	1 - 2	2	2.5
Loss on ignition..	14.0	NAP	NAP	26

NAP Not applicable. ¹Reference 49.

emphasis on using domestic raw materials and with the escalating cost of energy, an increasing interest has been shown in new aluminum producing technology.

Among potential domestic resources of aluminum, high-alumina clays appear to be the most favorable (36, 39, 50). In particular, the kaolinitic clay deposits in the southeastern United States are attractive because of their size, accessibility, and quality. The richest deposits, found in Georgia, are estimated to have resources in excess of 3 billion tons accessible to mining and processing (50). Such clay can be considered of high quality because of its high alumina content and because of its lack of complexing impurities. Composition of a typical high-quality Georgia clay is shown in table 1.

For processing purposes this clay can be considered as a mixture of silica, alumina, titania, and iron oxide chemically separable but not separable by mechanical means. The silica in the

quantities present can be considered a waste product, the titania a valuable by-product; and the iron a nuisance by-product. It is the qualitative differences between clay and bauxite that give the competitive edge to the latter.

If political and strategic considerations dictate the use of clay as a domestic aluminum source, it is conceivable to extract alumina suitable for reduction in existing primary aluminum plants (38). However, if this new resource is exploited it is also conceivable to extract the aluminum in a form suitable for reduction in a new, more energy efficient process. Recent patent disclosures and successful large-scale operation of an aluminum chloride reduction cell offer such a process (9, 17, 42, 44-45). There now exists a potential domestic resource and a developing, energy-efficient technology for producing aluminum; lacking is a proven technology for converting the kaolinitic clay into anhydrous aluminum chloride suitable for electrolytic reduction to metal.

TECHNICAL REQUIREMENTS

The nature of kaolinitic clay and the requirements for the aluminum chloride product should be examined before considering the chlorination process. Kaolinite, a hydrated aluminum silicate, consists of alternate single layers of Al_2O_3 and SiO_2 held together by the water of hydration. On a microscopic level, kaolinitic clay is seen to be made up of stacks of hexagonal sheets much like pages of a book (22). The major physical impurity is separate grains of quartz

sand. The iron and titanium impurities appear to be within the kaolin structure because they cannot be completely removed without chemical destruction of the parent kaolin.

The free and structural water associated with clay cannot be tolerated in a chlorinator. Under the reaction conditions water and chlorine as a chloride combine to give the corresponding oxide and hydrogen chloride, a waste product

that must be scrubbed from the exiting gases. For every one part of water nearly four parts of chlorine are thus wasted as hydrogen chloride. Therefore, raw clay must be dried of free moisture and calcined to remove the water of hydration. A calcination temperature of 700°C is required (12, 19). At this and higher temperatures, and depending upon time, atmosphere, and the presence of other substances, kaolinitic clay can become quite refractory to subsequent chlorination (25). Therefore, this step in clay preparation can be critical to the entire chlorination process and should be carefully considered.

The calcination step can also be used to fix the form of clay feed. The plasticity of wet clay and its strength after the removal of hydration water allow it to be made into any form from fine powders to pellets of any size and shape. Prior to calcination, catalysts and reductants may be added to assure intimate contact in the final feed. But as a good thing can be overdone so can the property of clay to make strong fired shapes become a disadvantage. If the final feed form is made too dense there is a reduction in accessible surface area where chemical reaction occurs and the rate of chlorination becomes exceedingly slow. In general, kaolinitic clay can be considered an ideal raw material with respect to preparation as a reactor feed, but the preparation itself must be carefully controlled so that the desirable characteristics are not lost before the feed enters a reactor.

It is important that the anhydrous aluminum chloride product of chlorination and subsequent purification processes be very pure (41). The aluminum chloride will be fed as a vapor or solid into the high-temperature, molten-salt electrolytic cell that discharges only recyclable chlorine gas and product liquid aluminum metal. All impurities entering with the aluminum chloride must exit with these two or build up in the cell, causing premature shutdown (17). Some impurities, notably oxides, would react with cell components causing deterioration of carbon electrodes.

Of course, small quantities of impurities such as iron, silicon, sulfur, phosphorus, and other metals can be removed in association with the product aluminum but these must be kept below rigid specifications (1). Likewise some gaseous impurities and reaction products such as carbon monoxide, carbon dioxide, and sulfur chlorides, can be removed in the chlorine stream. In addition, a system to circulate the molten salt electrolyte and filter out impurities prior to introduction into the cell, much like the oil system in an automobile engine, has been described in the patent literature (17). Any such system would, of course, require more expensive equipment, add to the complexity of operation, and increase costs. Preparation of feed for electrolytic reduction must keep the impurities to within a few hundredths of a percent (41) while processing aluminum chloride at tons per hour.

ALUMINUM CHLORIDE PRODUCTION

Several schemes for processing aluminum mineral resources to aluminum metal are shown in figure 1. At the far left is the traditional Bayer-Hall-Heroult combination; the double line branching from this indicates the path taken by the recent development and operation of a pilot production facility (43); and the dashed lines represent the possibilities of interest here. The latter two show a combination of chlorination and purification operations.

Going from right to left across the upper part of figure 1, the degree of purification prior to chlorination increases. At the far left the alumina intermediate is of sufficient purity so that the chloride produced from it may be used directly in reduction cells. The center path represents removal of nuisance impurities, such as iron, prior to chlorination. Attempts to remove iron from bauxite and clay indicate that this

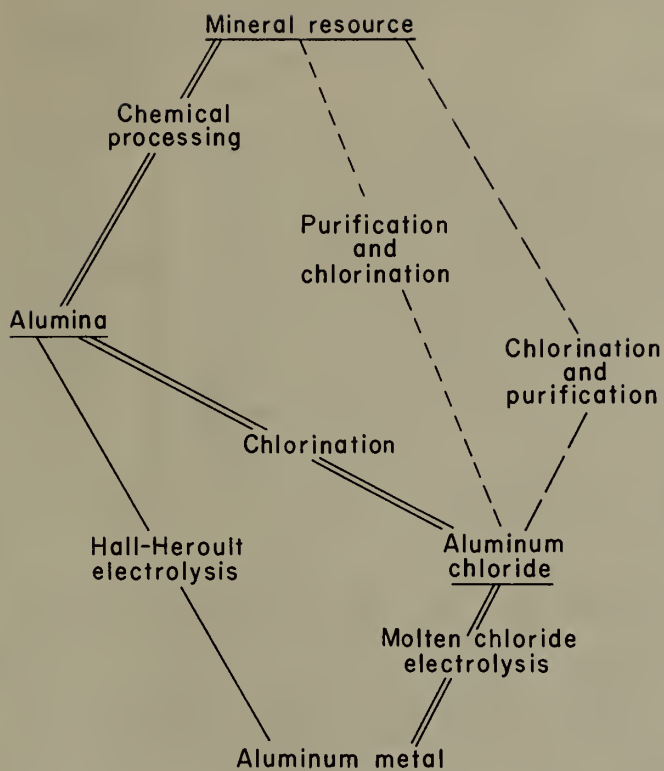


FIGURE 1. - Processing routes to aluminum.

does not now seem possible short of total chemical modification of the material such as in the Bayer process (7, 20, 32-33). Therefore, the following discussion will consider the path on the far right representing chlorination of domestic kaolinitic clay followed by purification of the anhydrous aluminum chloride product as outlined in the generalized flowsheet of figure 2.

CHLORINATION OF DOMESTIC CLAY

All of the metal oxides associated with domestic kaolinitic clay chlorinate in the presence of carbon as noted by the thermodynamic data in table 2 (28). (A negative value for the Gibbs function indicates that a reaction is possible at the temperature indicated.) Similarly, all of the chlorides will react with oxygen to give the oxides and free chlorine. Thus it would seem to be a simple matter to completely chlorinate the clay, separate the chlorides by fractional vaporization according to the vapor pressures shown in

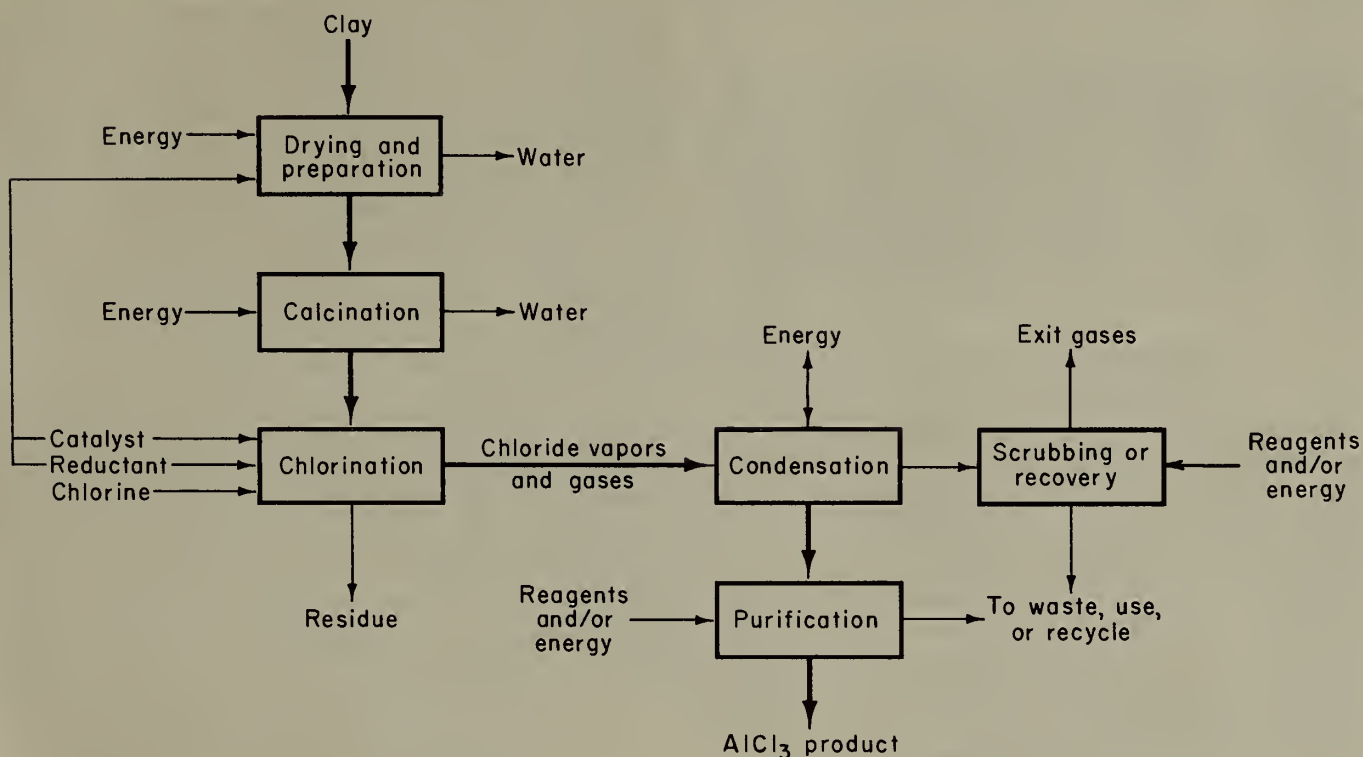


FIGURE 2. - Generalized process flowsheet.

TABLE 2. - Reactions pertinent to clay chlorination

Reaction	Enthalpy, $\Delta H_{900\text{ K}}$, kcal	Gibbs function, $\Delta G_{900\text{ K}}$, kcal
(1) $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \rightarrow [\text{Al}_2\text{O}_3 + 2\text{SiO}_2] + 2\text{H}_2\text{O}$	156.4	Nap
(2) $[\text{Al}_2\text{O}_3 + 2\text{SiO}_2] + 3\text{Cl}_2 + 1.5\text{C} \rightarrow 2\text{AlCl}_3 + 2\text{SiO}_2 + 1.5\text{CO}_2$...	-21.5	-66.1
(3) $[\text{Al}_2\text{O}_3 + 2\text{SiO}_2] + 3\text{Cl}_2 + 3\text{C} \rightarrow 2\text{AlCl}_3 + 2\text{SiO}_2 + 3\text{CO}$	40.0	-61.4
(4) $[\text{Al}_2\text{O}_3 + 2\text{SiO}_2] + 3\text{Cl}_2 + 3\text{CO} \rightarrow 2\text{AlCl}_3 + 2\text{SiO}_2 + 3\text{CO}_2$	-83.0	-70.7
(5) $[\text{Al}_2\text{O}_3 + 2\text{SiO}_2] + 3\text{COCl}_2 \rightarrow 2\text{AlCl}_3 + 2\text{SiO}_2 + 3\text{CO}_2$	-67.4	-73.9
(6) $[\text{Al}_2\text{O}_3 + 2\text{SiO}_2] + 7\text{Cl}_2 + 3.5\text{C} \rightarrow 2\text{AlCl}_3 + 2\text{SiCl}_4 + 3.5\text{CO}_2$..	-89.8	-154.8
(7) $\text{Fe}_2\text{O}_3 + 3\text{Cl}_2 + 1.5\text{C} \rightarrow 2\text{FeCl}_3 + 1.5\text{CO}_2$	-71.2	-115.4
(8) $\text{TiO}_2 + 2\text{Cl}_2 + \text{C} \rightarrow \text{TiCl}_4 + \text{CO}_2$	-51.8	-64.7
(9) $\text{SiCl}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{Cl}_2$	-60.8	-54.9
(10) $2\text{FeCl}_3 + 1.5\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{Cl}_2$	-74.6	-47.2
(11) $3\text{SiCl}_4 + 2\text{Al}_2\text{O}_3 \rightarrow 4\text{AlCl}_3 + 3\text{SiO}_2$	59.5	.9

Nap Not applicable. ¹At 298 K, for the water as vapor.

figure 3, reclaim the chlorine from the unwanted chlorides by reaction with oxygen, and electrowin aluminum chloride to the desired metal and recyclable chlorine (6). But the realities of the physical world are not so simple. These realities will be examined with reference to each operation, process, and output stream in the generalized flowsheet in figure 2 and the relative quantities of materials listed in table 3.

Although considerable energy is required to remove the water, both free and combined, which typically totals some 1.43 lb per pound of aluminum, clay preparation, drying, and calcination present no problems. As was stated earlier, care need only be taken to insure that the innate reactivity of the clay is not

destroyed in these operations. A solid carbon reductant and/or suitable catalyst can be added prior to calcination. Carbon added at this point must be very finely divided and evenly distributed because its reducing effect appears to occur only at the immediate clay-carbon interface.

The chlorination process itself is complex and several reactions occur simultaneously with the chlorination of the aluminum oxide portion of the clay. It is desirable to have this latter reaction proceed rapidly and completely, so that the reaction is as small as possible, and so that the chlorine is entirely consumed and need not be separated from the product gases and recycled. Although the negative value of the Gibbs function

TABLE 3. - Quantities of materials per pound of aluminum, pounds

Free water in wet clay (assumed, ~14 pct).....	0.76	Silicon tetrachloride ¹	6.05
Combined water.....	.67	Chlorine in silicon tetrachloride ¹	5.05
Oxygen associated with aluminum....	.89	Silicon dioxide residue ²	2.14
Reductant for aluminum oxide:		Iron.....	.059
Carbon, $\text{C} \rightarrow \text{CO}$67	Iron trichloride ¹17
Carbon, $\text{C} \rightarrow \text{CO}_2$33	Chlorine in iron trichloride.....	.11
Carbon monoxide, $\text{CO} \rightarrow \text{CO}_2$	1.56	Titanium.....	.050
Chlorine in aluminum chloride.....	3.94	Titanium tetrachloride ¹20
Aluminum chloride.....	4.94	Chlorine in titanium tetrachloride ¹15

¹Assuming total chlorination.

²Assuming no chlorination.

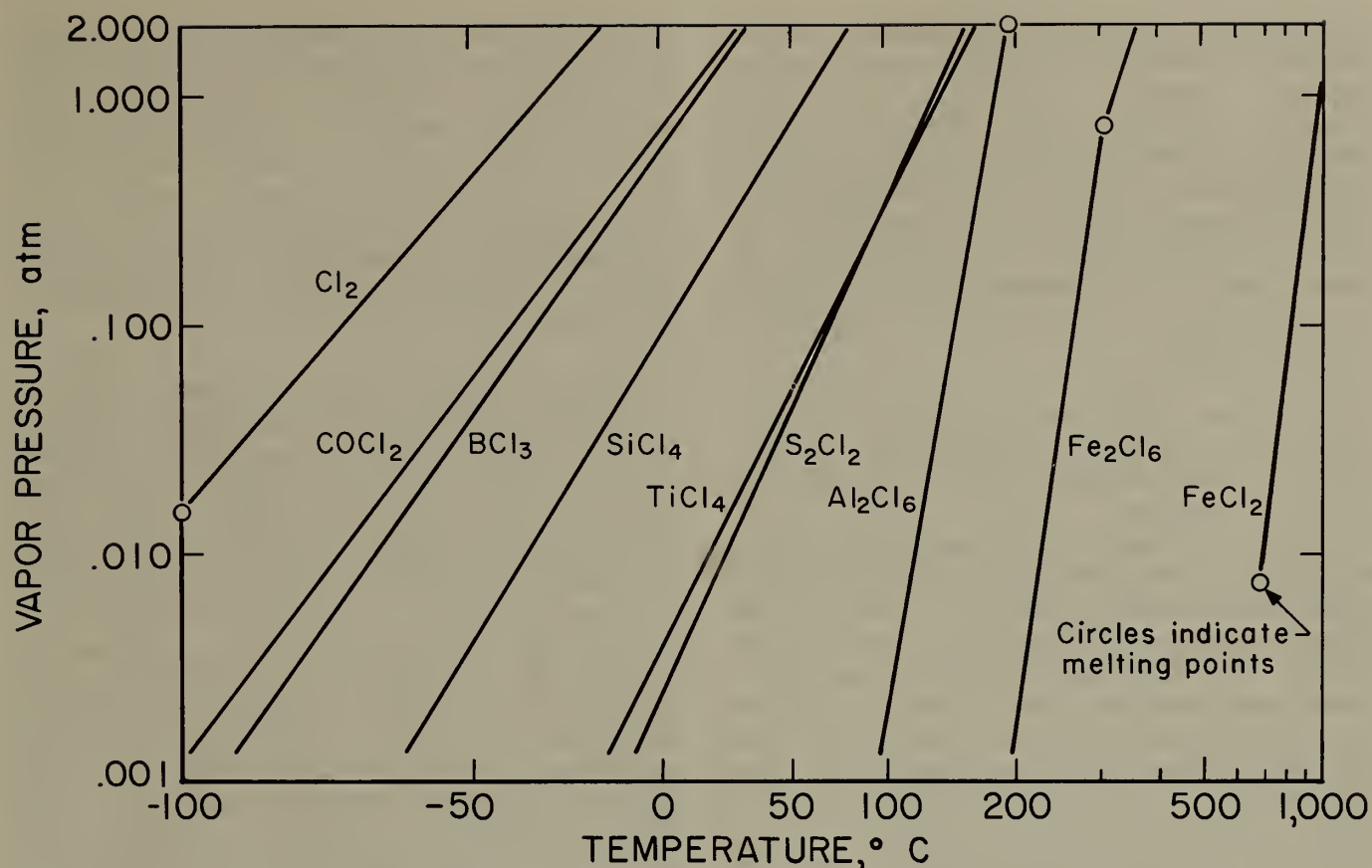


FIGURE 3. - Pertinent vapor pressures.

predicts that a reaction is favorable, it does not indicate the rate of the reaction. In order to obtain a sufficiently rapid reaction, a temperature of between 550° and 700° C is necessary (26). (Table 2 is based on 900 K or 627° C.)

In this temperature range, several catalysts have been reported to enhance the chlorination rate of the aluminum portion of clay. These include sodium chloride (26), boron trichloride (51), and sulfur compounds (52). Each of these increases the reaction rate of alumina but, with the exception of higher concentrations of boron trichloride, they do not appear to change the rate of silica chlorination. The net effect is therefore an apparent selective chlorination of alumina.

The mechanism by which these catalysts work continues to be investigated. It is known that sodium chloride and perhaps

boron chloride combine with some of the aluminum chloride product to form a liquid phase. These liquids are capable of dissolving small amounts of the aluminum oxide portion of the clay, and it is suspected that this dissolved aluminum oxide chlorinates easily and leaves as the volatile chloride.

The fate of the catalyst as well as its effectiveness is of importance. A sodium chloride catalyst could remain in large part with the unreacted residue. It would be necessary to remove this soluble salt before disposing of the solid residue. The sulfur and boron most likely would leave the reactor as obnoxious gaseous chlorides that require very low condensation temperatures (refer to figure 3) or efficient chemical scrubbing for their removal. If scrubbing is necessary the catalyst is not likely to be available for reuse (5). It is also possible that any of these catalysts

would combine with or be adsorbed on the condensed aluminum chloride product and require special removal procedures. Finally, the corrosive nature of the catalyst products needs to be considered with respect to equipment construction. Liquid phase sodium aluminum chloride could attack refractories in the reactor and the combination of sulfur and chlorine is known to be quite corrosive (34).

The carbon reductant used in the chlorination reaction must be chosen to fulfill several requirements. First, it must be reactive, i.e., it must sustain the desired alumina chlorination reaction with respect to rate and extent, and it should be somewhat selective towards the chlorination of alumina over silica. Carbon monoxide and phosgene best fill these requirements (see reactions 4 and 5, table 2; some silica does chlorinate but this is not indicated in the equation).

Solid carbons (reactions 2, 3, and 6) promote rapid reactions only if they are finely divided or have a high surface area characteristic of expensive activated charcoal (26). According to published data, solid carbon is less selective in promoting chlorination of the alumina over the silica portion of clay (26). However, elemental carbon has a higher capacity for reaction with oxides if the final product is carbon dioxide and therefore less carbon is needed (compare reactions 2, 3, and 4).

When handling and storage are considered, solid carbon would be the most desirable reductant. Extremely toxic carbon monoxide gas would have to be stored under pressure, requiring special precautions. Phosgene too is toxic but can be detected by its odor and immediate physiological effects. It has the advantage of being able to be stored as a liquid under reasonable pressure and incorporates both the reducing agent and chlorine in one compound.

The enthalpy of reaction is of considerable importance when selecting

the reductant. A chlorinator of the size to be used in the aluminum industry must be internally heated. External heating would require that the outer containment vessel be the hottest part of the reactor and any chlorinating agent reaching it would react violently with the metal at the temperatures required. With internal heating the outer vessel can be kept as cool as desired.

Heat can be generated within the reactor by feeding hot reactants, burning some of the carbon reductant with added oxygen, and by the chlorination reaction itself. Burning with added oxygen not only requires oxygen and more carbon but it also dilutes and adds to the volume of the product gases. The clay itself can be fed hot directly from the calcination step. As indicated by the values of enthalpy in table 2, only two of the important reactions occurring in the chlorinator, reactions 3 and 11, are endothermic and should be avoided. The carbon monoxide generated in reaction 3 would most likely be reacted further according to reaction 4. Reaction 11 will be discussed later.

Finally, the purity of the reductant need be considered. Hydrogen, sulfur, and alkaline metals and their oxides associated with some carbon materials would be detrimental. These would be chlorinated in the reactor leaving a sticky residue of the nonvolatile chlorides or add undesirable vapors to the exiting gas, and all would consume valuable chlorine. In this latter case small amounts of hydrogen are particularly wasteful because only one part of hydrogen combines with 35 parts of chlorine by weight to give hydrogen chloride.

Silica, being the predominant species in clay, requires special consideration with respect to conservation of chlorine. Even with the best selectivity reported for the preferential chlorination of the alumina fraction of clay, some silicon tetrachloride also is produced (26). With no market for the large amount that would be a byproduct of clay chlorination, disposal of silicon tetrachloride

would be necessary. This would not be easy because it readily hydrolyzes to silica and hydrogen chloride, a waste of valuable chlorine. Three solutions to this problem have been proposed.

The first and least acceptable is to scrub the exit waste gases containing the silicon tetrachloride vapor with a caustic solution, losing the chlorine value as salt. Another solution is to react the silicon tetrachloride with oxygen to give disposable silica and recyclable chlorine (27). An efficient, proven technology for this option is not now available. The third proposal is to recycle silicon tetrachloride through the chlorinator to take advantage of reaction 11 listed in table 2 (31, 41).

In the temperature range considered for a clay chlorinator, this reaction may go in either direction. At higher temperatures and higher concentrations of silicon tetrachloride, the reaction favors the formation of aluminum chloride. At slightly lower temperatures and higher concentrations of aluminum chloride, the aluminum chloride will react with silica to form silicon tetrachloride and alumina. Therefore, by proper selection of temperature and the amount of silicon tetrachloride fed with the incoming chlorine, it is conceivable to prevent further chlorination of silica in the chlorinator. Both of the latter methods require the recovery of silicon tetrachloride from the gaseous products. Condensation to accomplish this separation requires that the entire gaseous product stream be cooled to below 0°C and probably as low as -40°C where the vapor pressure for silicon tetrachloride is about one-hundredth of an atmosphere. Such a recovery system would require sizable equipment and considerable energy (53).

Even if it were economical to recycle silicon tetrachloride, circumstances have been found which could prevent its feasibility. It has been reported that clay exposed to silicon tetrachloride vapor at high temperatures becomes nonreactive with respect to chlorination (26).

Catalysts such as sodium chloride may reverse this condition (31).

The most attractive solution to the silicon tetrachloride problem is to limit its formation to a level where recovery of the chlorine value associated with this byproduct is not necessary. Limiting silica chlorination can be quite complex (30). In addition to the reductant and catalysts used, the chlorination reactor configuration can influence silicon tetrachloride formation (29). The operation of an ideal fluidized bed chlorinator illustrates this point.

The solid feed would consist of clay, a solid reductant, and catalyst. Chlorine would be the fluidizing gas. Outlet gases ideally would be only carbon dioxide and aluminum chloride vapor. Consequently, the solids overflow would consist of excess reductant, catalyst, and silica residue, with very little alumina. This is also the composition of the bed. Even though the alumina may be much more reactive than the silica, in this arrangement there is a much greater opportunity for the silica to react.

In contrast to the fluidized bed concept, a countercurrent reactor in which the gas stream flows counter to the solids could enhance selective chlorination of the alumina. Even though incoming chlorine would encounter reacted clay consisting primarily of silica, any silicon tetrachloride formed would have an opportunity to react with alumina in fresh clay as the gas stream left the reactor (reaction 11). On the other hand, the countercurrent reactor allows any silicon tetrachloride formed to pass over yet unreacted clay with the possibility of inactivation as mentioned above.

Clay chlorination in a liquid phase reactor with molten salts as the liquid and catalyst has been suggested (18). In this case, residual powdery silica from the unreacted clay would be difficult to separate and remove from such a reactor.

Whatever type of reactor is considered, a solid residue will be formed. Disposal

of this residue must be considered. Ideally the residue would consist of innocuous silica, but in practice there would also be some chlorinated products. These, especially any toxic chlorinated carbon compounds, would have to be destroyed or disposed of safely. The amounts and nature of such compounds depend upon the minor constituents of the clay, reductant, and catalyst and have not as yet been reported.

PURIFICATION OF ANHYDROUS ALUMINUM CHLORIDE

As it emerges from the chlorinator, product aluminum chloride is but a part of a mixture of gases and vapors from which it must be separated and purified. Under the most ideal chlorinator operation, represented by reaction 2 in table 2, aluminum chloride vapor would constitute only slightly more than half of the total volume of the product stream. Furthermore, at the temperatures necessary for condensation, aluminum chloride forms dimers and complex molecules as indicated in reactions 12 and 14 (35) of table 4. As such it would represent only 40 pct of the product volume (and pressure).

Therefore, according to the vapor pressures shown in figure 3, to recover by condensation 99 pct of the product at a total pressure of 1 atm, the temperature would have to be lowered to 114° C. This is about 75° C below the melting point of aluminum chloride. The above exercise in stoichiometry brings to light the two factors that complicate any process for purifying aluminum chloride: the tendency of aluminum chloride to form complex molecules with itself and other chlorides

and its high vapor pressure at its melting point (16).

It would not be practical to recover aluminum chloride as a liquid from chlorinator gases; the total pressure required is too high. Instead it would be condensed as a fluffy powder unless special conditions such as fluidized bed condensers were employed. The more dense, granular, more easily handled product of the fluidized bed condenser is preferred (23, 46). Because aluminum chloride is hygroscopic, it must not come into contact with atmospheric moisture and, therefore, any transport or storage between the chlorination and purification processes requires specially designed equipment. A free-flowing material such as the product of the fluidized bed would be advantageous.

As a first consideration, controlled condensation appears to be the solution to obtaining a pure aluminum chloride from the chlorination product stream (2). According to the simplistic presentation of vapor pressures in figure 3, the vapor pressures of aluminum chloride and ferric chloride differ by a factor of about 2,000, a ratio near the acceptable limit for iron in the aluminum chloride product. Two condensers in series would ideally deliver this product.

The first condenser, operating at about 190° C, would remove ferric chloride to an acceptably low level without condensing any aluminum chloride. The second condenser, held at 100° C, would remove essentially all of the aluminum chloride. Remaining in the gas exiting the second condenser along with the carbon dioxide and carbon monoxide, would be titanium

TABLE 4. - Reactions pertinent to aluminum chloride purification

Reaction	Enthalpy, $\Delta H_{500\text{ K}}$, kcal	Gibbs function, $\Delta G_{500\text{ K}}$, kcal
(12) $2\text{AlCl}_3 \rightarrow \text{Al}_2\text{Cl}_6$	-30.0	-12.8
(13) $2\text{FeCl}_3 \rightarrow \text{Fe}_2\text{Cl}_6$	-34.2	-17.2
(14) $\text{Al}_2\text{Cl}_6 + \text{Fe}_2\text{Cl}_6 \rightarrow (\text{AlFeCl}_6)_n$	± 1	± 1
(15) $\text{FeCl}_3 \rightarrow \text{FeCl}_2 + 0.5\text{ Cl}_2$	26.9	19.1

tetrachloride and any silicon tetrachloride, catalyst products, and unreacted chlorine. These chlorides could be condensed at a much lower temperature, subsequently separated from one another by fraction distillation, and used. If not recovered they would have to be scrubbed and disposed of as waste. There is no mention in the technical literature of difficulties in separating these lower boiling compounds from aluminum chloride; however, the separation of chlorides with low vapor pressures from aluminum chloride is reportedly not as simple as it might seem.

Separation of aluminum and ferric chlorides is complicated by the formation of the mixed dimer AlFeCl_6 according to reaction 14 of table 4 (47-48). This molecule and multiples of it have been reported from mass spectrometer observations of the vapor over mixtures of the two simple chlorides (11, 21, 35, 47). Measured properties of the mixed iron-aluminum chloride indicate that its vapor pressure and the equilibria for reaction 14 are such that the iron is more intimately associated with aluminum chloride than would be expected from simple vapor pressure data. There is a tendency for the mixed chloride to form and its vapor pressure appears to be closer to that of the aluminum chloride dimer than is the vapor pressure of ferric chloride.

Considerable effort has been put into developing a scheme to separate iron and aluminum chlorides but, notably, success of suitable technology for the solution to this problem has not been reported in the literature. Although fractional distillation, fractional sublimation, and reduction of ferric chloride to less volatile ferrous chloride have been suggested, the operation of a practical scheme to separate iron chloride from aluminum chloride has not been reported.

Reducing the iron chloride to the less volatile ferrous chloride or iron metal followed by separation by volatilization

of the aluminum chloride may be possible (4) if the appropriate reducing agent can be found (8). Aluminum metal is a prime candidate for the reductant since it would not add another material to the system, only more aluminum chloride. It is, however, an expensive reagent and there are technical problems. If solid aluminum is used (i.e., if the reduction is carried out below 660°C) large surface areas of aluminum are needed to contact the liquid or vapor aluminum chloride-iron chloride mixture. This surface soon becomes covered with reaction products and loses its reactivity. If the impure aluminum chloride vapor is passed through molten aluminum in order to reduce and remove the iron impurity, high melting iron-aluminum intermetallic compounds form. These solids in the molten aluminum bath quickly hinder the operation.

Fractional sublimation on a large scale has never been a success owing to the difficulties inherent in the mechanics of moving large quantities of condensing solids. In the case of aluminum chloride the strict avoidance of contact with the atmosphere would only add to these difficulties.

Although other schemes have been proposed (40), fractional distillation is the most attractive method for separating ferric chloride from aluminum chloride. The feasibility of this operation depends upon the nature of the vapor-liquid equilibria for the binary system, for which there are yet no data in the literature.

Finally, there are minute quantities of other elements such as calcium, magnesium, and phosphorus that have not been considered. These may present problems as impurities which associate with the aluminum chloride (10). Only extended pilot scale operation of an aluminum chloride-from-clay process could identify the importance of these potential impurities.

CONCLUSIONS

There is a strategic incentive in the United States to use domestic clay as a resource for aluminum; and there is an economic incentive to develop a chloride metallurgy to produce aluminum from the clay. Together these make the chloride route from clay to aluminum attractive and worthy of serious consideration. However, there are several basic problems to be investigated and much development work to be done before it can be determined if such a technology can in fact be made practical and economical on a large industrial scale. Only a sustained, well coordinated research and development effort can provide the data needed for technical and economic evaluations of any proposed chloride route for aluminum from clay.

At the present time two areas need to be addressed: the clay chlorination

reaction and the purification of anhydrous aluminum chloride. In particular, the chlorination reaction must be understood so that it can be assessed with respect to rapid and complete use of chlorine; selectivity of alumina reactivity over silica; use of a convenient, inexpensive reductant; and heat generation to sustain the reaction.

In addition, the identity and nature of product impurities and their interactions with anhydrous aluminum chloride must be determined. With such information a chlorination process and purification scheme can be proposed and tested. Only then will the technical operation problems surface; and only if these can be solved with due regard to economic considerations will the chloride route from clay to aluminum become industrially possible.

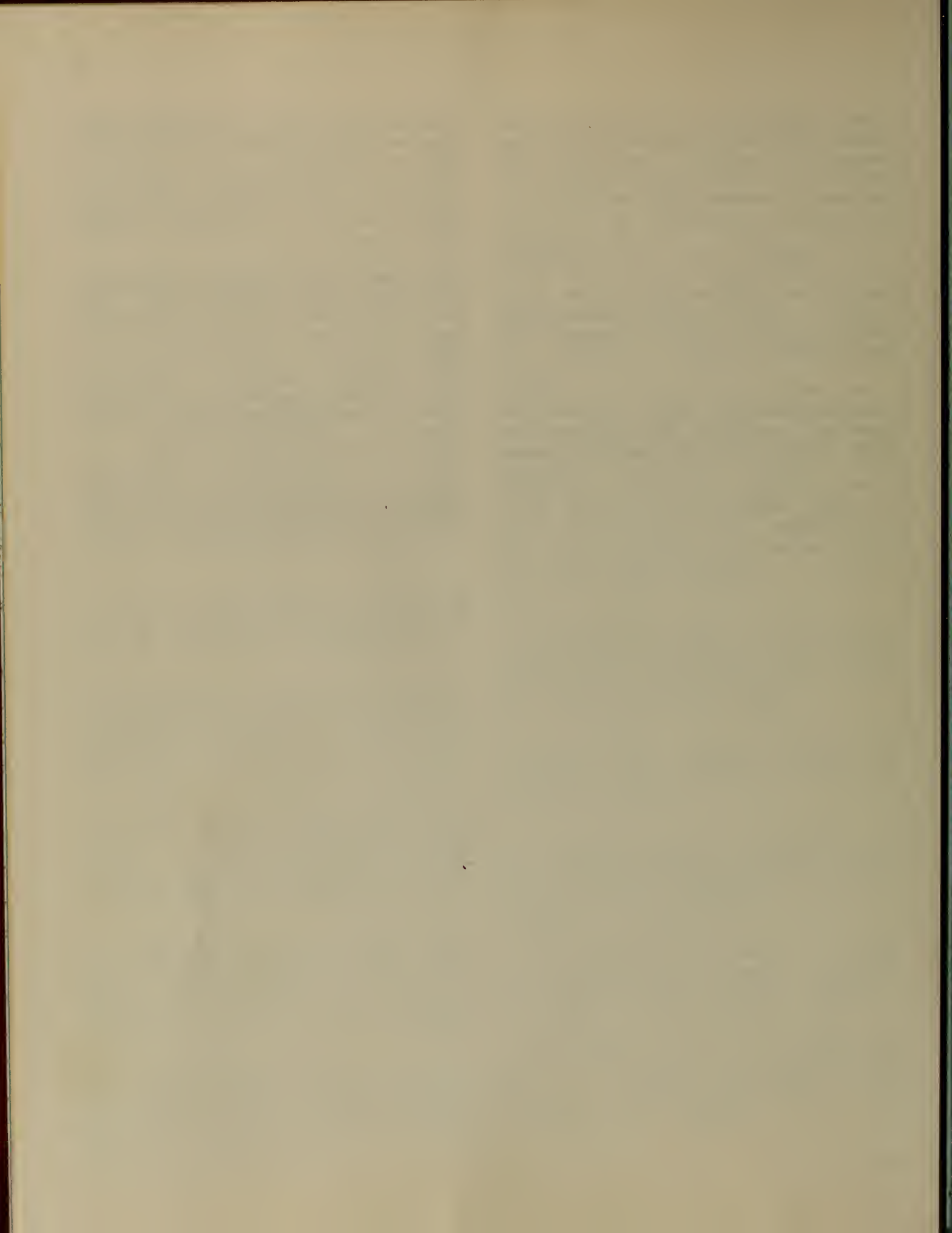
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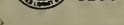
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